DELHI COLLEGE OF ENGINEERING

BAWANA ROAD DELHI-42

LIBRARY

Class No ____________________

Book No ____________________

Accession No ____________________

STUDY ON TACKIFYING RESINS AND THEIR DISPERSIONS

A dissertation submitted
in Partial fulfillment of the requirement for the award of the degree of

Master of Engineering

POLYMER TECHNOLOGY

MANOJ KUMAR BHARDWAJ

Dr. A.P. Gupta

DEPARTMENT OF APPLIED CHEMISTRY
DELHI COLLEGE OF ENGINEERING
NEW CAMPUS, BAWANA ROAD, NEW DELHI
APRIL 2001

CERTIFICATE

This is to certify that minor thesis entitled **"Study on tackifying resins and their dispersion"** submitted by **Mr. Manoj Kumar Bhardwaj** to **Delhi College of Engineering, Delhi** for the award of degree of **Master of Engineering** in **Polymer technology** is a record of Bonafied research work carried out by him. **Mr. Manoj Kumar Bhardwaj** has worked under our supervision & has fulfilled the requirement for the submission of this dissertation, which to our knowledge has reached the requisite standards.

Dr. A.P. Gupta
Professor,
Deptt.of Applied chemistry,
Delhi College of Engineering,
Delhi

Dr.G. L. Verma
Professor & Head
Deptt.of Applied chemistry,
Delhi College of Engineering,
Delhi

Dr. Jagbir Singh
Manager, R&D,
Vam Organics
chemicals Ltd
Sahibabad. (U P.)

ACKNOWLEDGEMENT

It is my great pleasure to express my profound to my guides **Dr A.P. Gupta** (Professor, Department of Applied chemistry, Delhi College of engineering, Delhi) and **Dr. Jagbir Singh** (Manager, R&D, Vam Organics Chemicals Ltd., Sahibabad, U.P.) for their inspiring guidance and encouragement through out this minor project work. The discussion held with them was much enlightening and motivated me to work with greater zeal and enthusiasm.

I pay my sincere thanks to **Dr.G.L. Verma, Prof.& Head, Department of Applied Chemistry,** for their kind help.

I also wish to acknowledge the support extended by **Dr. Mukul Jain** and **Mr. Arvind Kumar** and all the staff of **V.O.C.Ltd.Sahibabad, U.P.**

A word of thanks to my friends and colleagues for their forbearance and mutual help provided by them, which is a must for the successful completion of any project work

Above all, I am grateful to my Parents without whose blessings and constant help this work would not have been possible.

April 2001 **(MANOJ KUMAR BHARDWAJ)**
Delhi

INTRODUCTION

All areas of the chemical industry have been affected by regulatory changes over the last 10 years. Nowhere have these changes been more apparent than in the adhesive industry. These environmental pressure, along with economic pressure, have lead to the great changes in the relative amount of solution, emulsion, and hot melt adhesive being used by the adhesive industry. Raw material supplier aware of, and respond to, these changes in technology. A part of development activities of several resin suppliers over the last few years has therefore been the development of resin dispersion for adhesive emulsions.[1]

There are many advantages to using aqueous systems. In addition to the environmental economic factors, existing equipment used for solution adhesives can be utilized for aqueous emulsion systems. . Aqueous emulsion adhesives are easily compounded and cleaned up and are safer to work with than solvent system. A wide range of raw materials are now available in aqueous emulsion form. However, mechanical, chemical and freeze - thaw stability are concerned with aqueous adhesives. In addition to resin polymer compatibility, the compatibility of emulsifier system must now be taken into consideration. The particulate nature of the components and the need for particle fusion must also be considered. However, even with these complicating factors, aqueous adhesives offers definite advantages and are an excellent alternative to solution systems.

Tackifier resin: Tackifier resins are the materials added to elastomers to improve pressure sensitive adhesion. They generally have molecular weight

in the range 500-2000,with broad molecular weight distribution. Their softening point vary from 50 -150^0C and often have rather limited compatibility with elastomers to which they are added.

The properties of a pressure sensitive adhesive depend primarily on the viscoelastic nature of the adhesive mass. A pressure sensitive adhesive formulation, an elastomer or rubbery polymer provides the elastic component. While a low molecular weight tackifying resin constitutes the viscous component. Thus, for any given elastomer system, it is the tackifying resin that ultimately determines the viscoelastic behavior & the final properties of the finished adhesive.[2]

Types of tackifier resins: -

There are two major classes of tackifier resins. They are the **rosin derivatives** and the **hydrocarbon resins.** The rosin derivative class consists of rosins, modified rosins and various rosin derivatives, primarily rosin esters. The hydrocarbon rosin class consists of low molecular weight polymers produce from a wide variety of monomers derived primarily from petrochemical sources.

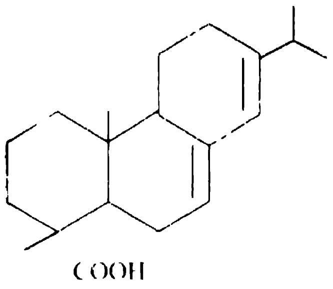
(1) Rosin and rosin derivatives :-

Rosin is a thermoplastic acidic resin obtained from pine trees. There are three major methods for obtaining rosin and the resulting product is named according to process that are used.

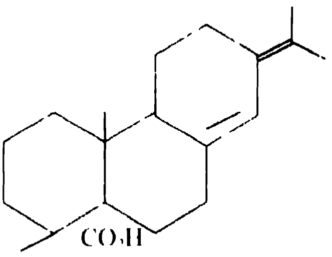
Gum rosin along with turpentine is obtained as oleoresin from living trees. This harvesting procedure, also called turpentining, involves

Figure: 1

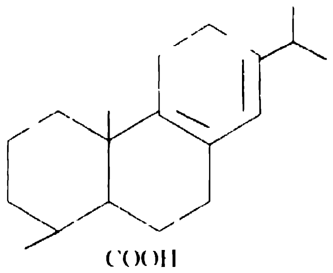
ABIETIC TYPE ACIDS



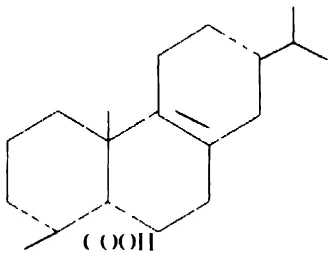
ABIETIC ACID



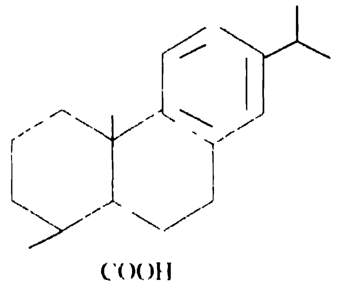
NEOABIETIC ACID



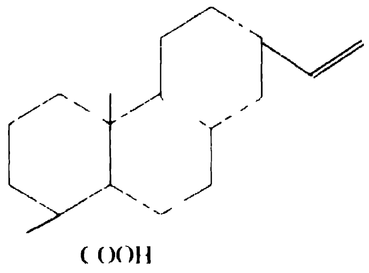
PALUSTRIC ACID



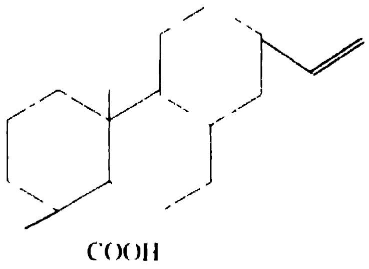
DIHYDROABIETIC ACID



DEHYDROABIETIC ACID



PIMARIC ACID



ISOPIMARIC ACID

PIMARIC TYPE ACIDS

wounding the tree and collecting the oleoresin that exude from wound. Sulphuric acid is used to enhance exudation and increase the yield of oleoresin. More recently, other materials, such as herbicide paraquats , have been found to further increase the yield of oleoresin as well as resinous content of the wood in the lower portion of the tree.[1] The oleoresin obtained from the process is than distilled to give gum rosin and turpentine.

Wood rosin is obtained from the aged pine stumps that are pulled up, washed and mechanically reduced to chip form. These chips are than extracted with solvent followed by distillation and further refining to give wood rosin.

Tall oil resin is the third type of rosin, and it is obtained from the tall oil, which is a byproduct of paper industry. During the pulping operation, wood chips are cooked under heat and pressure in alkaline medium. The pulp is removed by filtration and washing and the liquid portion is concentrated resulting in a precipitate that is removed and acidified to give crude tall oil. This crude tall oil consists mainly of fatty acid and rosin acids, which are separated by distillation.

Rosin from any of these three sources is a mixture of organic acid called rosin acids. Minor component consists of rosin ester and anhydrides, unsaponifiable matter, and fatty acids.

The rosin acids can be divided into two different types. These are the abietic acid type and the pimaric acid type, and unmodified rosin consists primarily of abietic acid. Figure 1 shows some of the more common members of these two types. It can be seen that differences in the two types

is the substitution pattern at the C-13 position. Abietic acid have an isopropyl group , while the pimaric acid have a methyl and a vinyl group.

Rosin by itself is generally unsuited for use in modern adhesive system because it is subjected to oxidation and other reactions as well as crystallization. Because of these, most rosin for adhesive use have been subjected to one or more of a series of reactions to form modified rosin or rosin derivatives. Among the more important reaction for the production of material for use in adhesives are disproportionation, polymerization, hydrogenation, and esterification.

Disproportionation takes place when rosin is heated to about 270^0C. The reaction may be accelerated by the use of various catalysts such as platinum or iodine. The result is a hydrogen exchange between the rosin acids where, for instance, two abietic acids are converted into dihydroabietic acid and a dehyroabietic acid.

Polymerization is affected by treating a solution of rosin in an inert solvent with an acid catalysts such as boron trifluoride or Sulphuric acid. Removal of the catalyst and solvent result in a product composed largely of rosin dimer and having a higher softening point than unmodified rosin.

Hydrogenation using Raney nickel or a similar catalysts can be tailored to give products that are only partially saturated, such as dihydroabietic acid, or completely saturated, such as tetrahydroabietic acids.

Rosin acid react with a variety of alcohols to form a ester. Because of steric hindrance, however the esterification requires rather high temperature, but the resulting esters are quite stable and resistant to hydrolysis. Usually polyhydric alcohols are used for esterification in order to give products with higher softening point and that are more polymeric in nature. Ethylene glycol, glycerol and pentaerythritol are the most common alcohols employed for this purpose. When stability is desired rosin esters are produced from the hydrogenated rosin.

Few examples of rosin based tackifier resins used in pressure sensitive adhesives are glycerine rosin esters, hydrogenated penterythritol ester, hydrogenated glycerine esters, modified tall oil rosin, polymerized rosin and rosin ester.

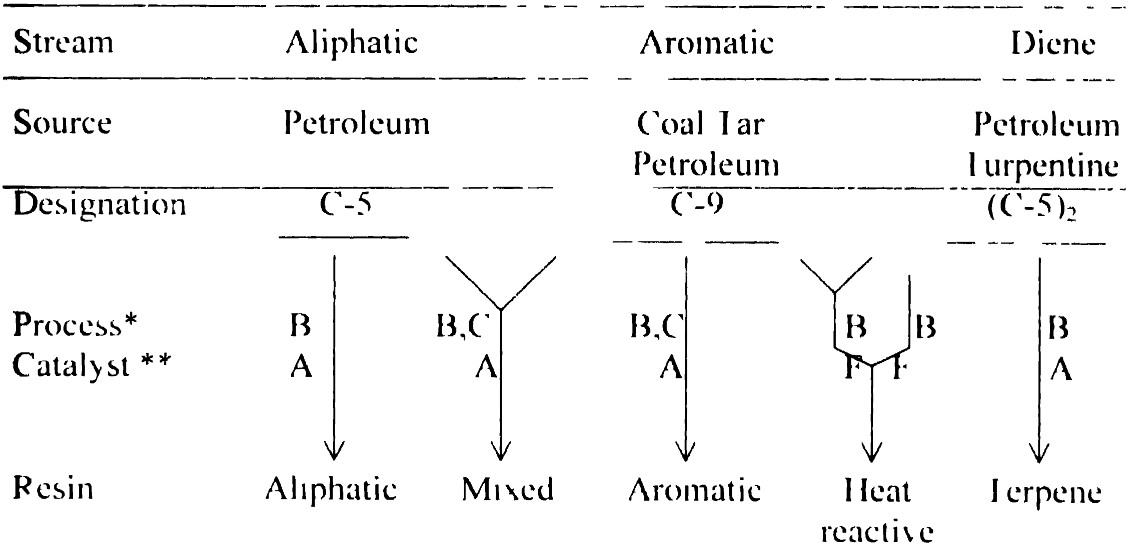
(2)Hydrocarbon Tackifier resins: -

Hydrocarbon tackifier resins are low molecular weight polymers derived from monomers obtained from petroleum, coal, and wood. Unlike the rosin derivatives, hydrocarbon resins are true polymers and monomer composition, polymerization methods, and final product molecular weight determine their performance characteristics.

Chemically , hydrocarbon resin streams may be classified as containing primarily aromatic , aliphatic and diene (cyclic olefin) monomers. These are also reffered to as C-9,C-5, and $(C\text{-}5)_2$, respectively, corresponding to the average number of carbon atoms per monomer molecule. Polymerization of these streamsis carried out using a lewis acid

catalyst or by a free radical process using heat and pressure. These streams, Polymerization methods, and the general designations of the resins produced are shown in figure 2.

Because of the variety of feed streams available and the various polymerization techniques that are employed, a wide variety of hydrocarbons resins are available with a broad range of properties and prices. Furthermore, It is this diversity that has made hydrocarbon useful in so many tackier applications, especially those involving pressure sensitive adhesives. The following discussion briefly treats each of the main types of hydrocarbon resins. The typical range of properties available will be outlined.



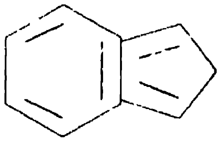
*B =batch process C= continuous

**A=Lewis acid catalyst (cationic) F=free radical –heat and pressure

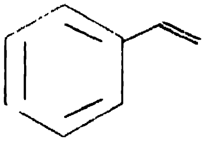
Fig.2 Hydrocarbon resins

Figure : 3

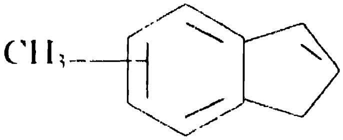
AROMATIC RESINS



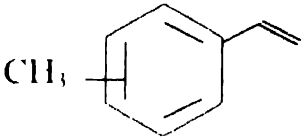
INDENE



STYRENE



METHYLINDENE



METHYLSTYRENE

(3)Aromatic Hydrocarbon Resins:-

The aromatic resin group [Fig. 3] consists of aromatic petroleum resins and resins from coal tar commonly called coumarone-indene resins. These resins are produced by the cationic solution polymerization of aromatic crude streams containing indene as the principal polymerizable monomer along with varying minor percentages of styrene, methylindene, and methylstyrenes. Coumarone or dicyclopentadiene may also be present depending upon the raw material source.

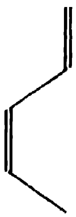
Aromatic Resins can be obtained in varying softening points from about 10^0C to over 150^0C and in colors ranging from pale straw to dark amber. The iodine number, which is generally taken as a measure of reactivity or unsaturation, is relatively low in these resins, ranging from 30 to 60. The specific gravities of aromatic resins are greater than 1.0, and usually fall in the 1.05 to 1.15 range. Finally, number -average molecular weight generally varies with the softening point and falls in the range of 290 to 1150.

Aromatic resins have a wide utility in a number of end use areas. Because of their excellent compatibility with most synthetic elastomers, they can be used as tackifier in a variety of contact cements mastics, and construction adhesives. The high softening point grades are finding increased use in adhesives based on the thermoplastics elastomers. They associate with the stryene end blocks, and can thus be used to modify the strength, viscosity, and upper service temperature of the adhesive blend.

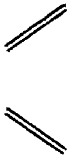
Aromatic resins are also used in the production of +inks various coatings as well as in rubber compounding, where they serve as process aids, plasticizers, and tackifiers

Figure : 4

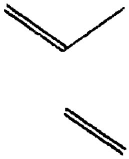
ALIPHATIC RESINS



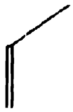
Cis-PIPERYLENE



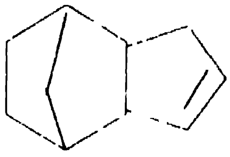
trans-PIPERYLENE



ISOPRENE



2-METHYLBUTENE-2



DICYCLOPENTADIENE

(4)Aliphatic Hydrocarbon resins:-

Aliphatic resins [Fig. 4] are produced from light, So called C-5 petroleum Fractions. The petroleum monomers are *cis*- and *trans*-piperylene. Also found in these streams are varying amounts of isoprene,2-methylbutene-2, and in some cases,dicyclopentadiene. These streams are polymerized using aluminium chloride, and the softening point is controlled by adjusting the composition of the diluent or monomers. This differs from the production of aromatic resins using BF3 the where softening point is controlled by changing the reaction conditions or the addition of plastisizer oils.

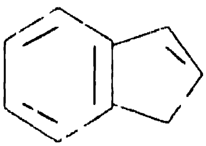
Aliphatic resins are generally available only in softening point grades from 80^0 C to 115^0 C because of production and demand limitations. An exception is a liquid resin, Wingtack 10,produced by Goodyear tire & Rubber company. The specific gravities of these resins are below 1.0,usually in the range of 0.93 and 0.98,and molecular weight run from 1000 to 1500, which is quite high when compared to other types of resins of equivalent softening points.

The aliphatic or C-5 resins have been available for many years. They were used primarily in rubber compounding, floor tile production, and some coating applications. The high quality grades that are currently available, however, are relatively recent innovations. These new generation C-5 resins are sometimes referred to as synthetic polyterpene resins to give an indication of their outstanding properties. They posses excellent heat stability and Very light polyethylenes, amorphus polypropylene, and they are outstanding tackifiers for natural rubber, *cis*-polyisoprene, and styrene-isoprene block copolymers. These properties combine to make these resins useful in the formulation of a wide variety of hot melt adhesives and

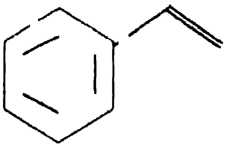
Figure : 5

HEAT REACTIVE RESINS

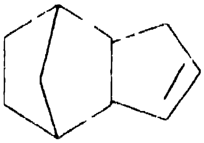
INDENE



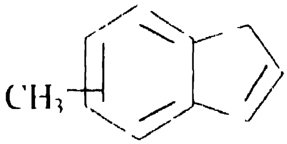
STYRENE



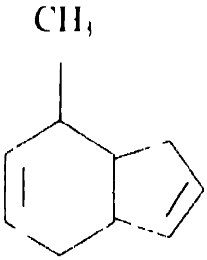
DICYCLOPENTADIENE



METHYLDICYCLO-
PENTADIENE



C-5 DIMERS



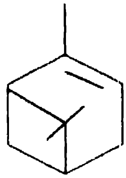
coatings as well as solvent-applied and hot melt pressures sensitive adhesives. They can also be used as light colored tackifiers and plasticizers in compounding a variety of types of elastomers.

Mixed Aliphatic/aromatic resins

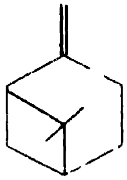
The mixed C-5/C-9 resins are hybrid resins produced by blending C-5 and c-9 streams in varying proportions and then polymerizing with either $AlCl_3$ or BF_3 as required. These resins are usually produced in only one or two softening point grades, and the properties obtained are generally intermediate between those of either straight aromatic or aliphatic resins. These resins are the result of research efforts by various manufacturers to fine-tune the compatibility and tackifying characteristics of their C-5 resins to produce product with outstanding performance in the hot melt and pressures sensitive adhesives.

Heat Reactive Hydrocarbon Resins

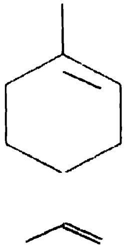
The next general class of hydrocarbons resin is the so-called heat reactive or diene resins [Fig. 5]. These are petroleum resins with a mixed aromatic and aliphatic composition. The stream used to produce these resins contain indene and styrene, mentioned before, along with substantial amounts of dicyclopentadiene, dimethyl-dicyclopentadiene, and various other C-5 dimers, better known as diene dimers. These resins are generally polymerized by action of heat and pressure in a free radical process. This method of polymerization is generally less costly than the use of a Friedel-



α-PINENE



β-PINENE



DIPENTENE

TERPENE RESINS

Figure : 6

Crafts catalyst, and the resins are, therefore, usually less expensive than the catalytic resins.

Colors of the heat reactive resins can vary from light pale yellow to dark amber. The iodine number of these reactive resins are quite high, ranging from about 120 to 220,depending on the feed blend and the actual polymerization conditions employed. Specific gravities are similar to those of aromatic resins, ranging from 1.08 to 1.10,and the molecular weight generally fall between 500 and 800.softening points of various grades usually fall between 95^0 and 140^0C, although some resins with higher values are available for special applications.

Because of the lower cost and excellent compatibility characteristics of these resins, they are widely used in compounding low cost adhesives such as cements, mastics, sealents, and even some solvent-applied pressure sensitive adhesives. Because of their reactivity they are subject to oxidation, however and an adequate stabilizer system should be used where long-term oxidation resistance is required.

Terpene Resins

Along with the heat reactive resins, the terpene resins [Fig. 6]may be classified as diene or $(C\text{-}5)_2$ resins, the monomer used in their production may be considered to be dimers of isoprene. Unlike the heat reactive resins, terpene resins are produced by cationic solution polymerization of raw materials obtained from turpentine and other natural sources, including citrus peel. The actual monomers are usually one or a combination of the terpenes: α-pinene,β-pinene, and dipentene or limonene. The catalyst is usually $AlCl_3$, although other Lewis acids can be used.

Terpene resins are light in color and can be obtained in softening points from 10^{0}C and 140^{0}C.The specific gravities range from 0.97 and 1.00 and molecular weights from about 300 and 2000. Generally speaking, at equivalent softening points, β-pinene resins have the highest molecular weights and lowest gravities, while dipentene resins have the highest gravities and lowest corresponding molecular weights.

Terpene resins, especially β-pinene resins, were the resins of choice in the production of pressure sensitive adhesives for many years. These resins have outstanding tackifying abilities when used with natural rubber wide range of softening points to choose from, and extremely broad food and Drug Administration clearances. More recently, limonene and limonene styrene copolymer resins have been developed that are almost water white or colorless.they are excellent tackifiers for butadiene-based elastomers and have become very popular for use in adhesives for the disposable products markets. Over the last ten years however, due to rising cost and uncertain availability, the terpene resins and rosin derivatives have lost considerable ground to the growing number of less expensive synthetic hydrocarbon resins designed specifically to replace them.

Modified or Special Resins

The final group of resin to be discussed are the so called special or modified resins. This is a catchall group used for resins having special properties that do not quite fit into the general class of resins. These resins are prepared by various techniques and by blending selected feed streams or pure monomers to obtain resins with special solubility, compatibility, or performance characteristics. The examples of Modified or special resins are:

- Hydrogenated resin
- Terpene Phenolic resin
- Vinyltoluene/α-methylstyrene
- Alkylated aromatic resin
- Phenol modified aromatic resin
- Acid modified resin

Fundamental Properties of a good tackifying resin:-

(i) It must be reasonably compatible with the base adhesive polymer. Compatibility between the tackifiers resin and elastomers is necessary to achieve mixing at the molecular level required to produce modified viscoelastic properties.[3]

(ii) It must have a very low molecular weight relative to the base elastomers. The low molecular weight is necessary to impart the viscous flow characteristic required by the adhesive blend to form bond quickly at low deformation or strain rates.[3]

(iii) It must have a glass transition temperature T_g that is higher than that of the base elastomers. Indeed most tackifier resins are brittle glassy solids with T_g values above room temperature in the range of 32 - 60°C.The high T_{gs} of the resin raises the T_g of the adhesive blend imparting stiffness. This gives the adhesive resistance to flow at high strain rates, thus making bond more difficult.[3]

Dispersion Technology

A dispersion is a two-phase system in which one phase consist of finely divided particles distributed throughout a bulk substance, the particle being the disperse or internal phase and the bulk substance the continuous or external phase.[4] A dispersion typically consists of a solid disperse phase and a liquid continuos phase. An emulsion consists of both a liquid disperse phase and a liquid continuous phase. Oil-in-water emulsions have oil as the disperse phase and water as the continuous phase. Water-in-oil emulsions have water as the disperse phase and oil as the continuous phase. Emulsifiers or surfactants are used to facilitate the emulsification and to promote emulsion or dispersion stability.

Surfactants are classified as anionic, cationic or non-ionic according to the charge carried by the surface-active part of the molecule.[5] An anionic surfactant will ionize in a solution to yield a large negatively charged ion and a small positively charged ion.[6] The anionic surfactant derives it's name from the surface active anion. Anionic surfactants can be further subdivided into general categories based upon chemical structure: sulphates, alkyl sulphonic acids and their salts, carboxylic acids and their salts, alkylaryl sulfonic acids and their salts, and misc.

Cationic emulsifiers will ionize to form a large positively charged ion and a small negatively charged ion. They can be subdivided into primary, secondary or tertiary amine salts, quaternary ammonium compounds and misc. Amphoteric (or ampholytic) surfactants assume either an anionic or cationic character. The ionic character of Amphoteric surfactants is a function of the pH of the system.

Resins can be emulsified or dispersed in two general ways:

1.) **Direct method and**

2.) **Inversion method.**[7]

In the **Direct method**, if the material is a liquid at room temperature, it can be dispersed directly into water using an emulsifier and agitation. If it is solid at room temperature, the resin can be dispersed at an elevated temperature where it is molten. Alternatively, The resin can be dissolved in a solvent; the resulting solution can be then emulsified. In this case, the solvent must be removed after emulsification in order to have a solvent free or low solvent dispersion.

In the **Inversion method, a** water-in-oil emulsion is first formed by slowly adding water to the oil phase in the presence of an emulsifier. As more water is added, the mixture eventually becomes thick at the inversion point where the water becomes the continuous phase.the fine particle size is developed by shearing the various mass at the inversion point. After inversion, additional water lowers the percent total solids of the dispersion.

PHYSICAL PROPERTIES OF RESIN DISPERSION

Properties of importance for a resin include the following

- Percent total solids
- pH
- Viscosity
- Particle size
- Ion tolerance

- Mechanical stability
- Freeze-thaw stability and
- Shelf stability

A discussion of several of these properties as they relate to the use of resin dispersion in aqueous adhesive system follows.

As mentioned earlier, the compatibility of resin-polymer emulsifier system must be taken into consideration with emulsion systems. When blending a resin dispersion with a polymer latex, it is advantageous to use products having similar emulsifiers and pH.however, similarity of pH is not an assurance of compatibility, or does dissimilarity mean initial incompatibility or poor stability of the aqueous blending on aging. The specific components of the blend should be checked for compatibility.

Ion tolerance indicates stability of a dispersion in the presence of electrolyte or extreme of pH. For example, anionic resin dispersions formed with fatty acids and rosin acid soaps have fairly high pH's, and therefore would be unstable when mixed with acidic latexes. Dispersion stability can be improved through poststabilization with certain nonionic surfactants. Dispersions of this type are refereed as ion tolerant.

Viscosities of the resin dispersion and of the blended adhesives are important in the mixing and coating processes. Different application methods have different requirements for aqueous adhesives viscosity.

The particle size of a resin dispersion can be measured by a variety of methods .It is believed that similarity of resin dispersion and polymer latex particle size promote better mixing and fusion of particles.

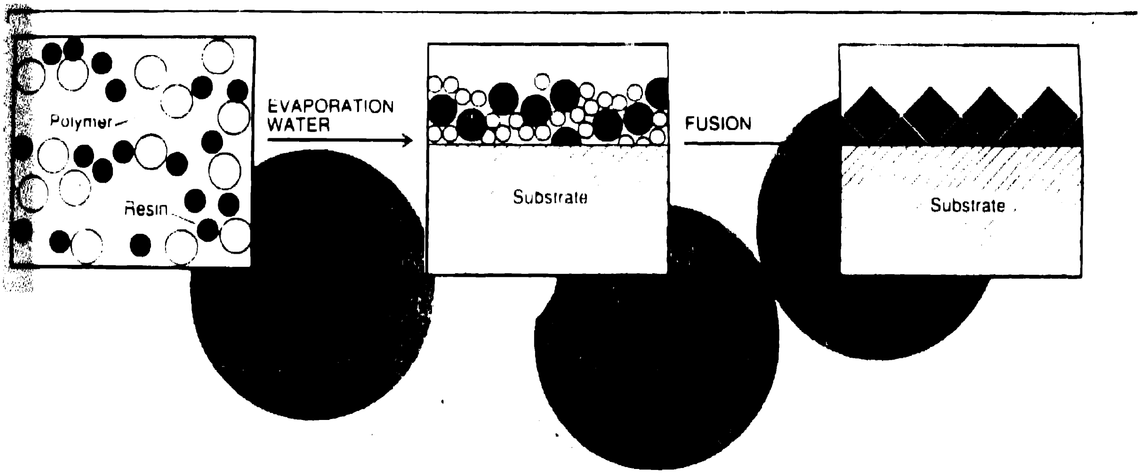


Fig. 7 MIXING AND PARTICLE FUSION

Other forms of dispersion stability are also important. In general, most resin dispersions must be protected from freezing.most have a limited shelf life, typically six months to a year, but this is dependent on the specific product.

Mechanical stability of both the resin dispersion and the formulated adhesive is necessary in order for both to survive shipping and processing. Shear forces will be encountered during mixing, pumping, and at the nips of the roller during coating.

Water resistance is another property of concern, particularly with emulsion systems. Most base resins and polymers are considered water insoluble. However, the water resistance of dried adhesive film is largely determined by the emulsifier system used in producing emulsions of the resin and polymer. Resin dispersions prepared from certain emulsifier offer more resistance to rewetting than others rewet.

The presence of emulsifiers in an aqueous system would also effect the migration or bleed resistance of the adhesive. Certain emulsifiers might eventually migrate to the adhesive-substrate interface and cause loss of adhesion .An emulsifier could possibly migrate into a porous substrate, such as label stock. These properties should be kept in mind and tested for with a specific adhesive system in a specific application. An emulsifier could also cause foam generation during application. Care must be taken if defoamers are used, in order to avoid any detrimental effect by the defoamers on adhesive properties.

Another concern specific to resin dispersion/polymer latex systems that of mixing and particle fusion .in solution adhesives, the adhesive components are mixed on a molecular basis.[7] Therefore, when the solvent is

evaporated the adhesive components are as finely mixed as possible in the dried film. In an aqueous adhesive mixture of resin dispersion and polymer latex, each component is present in individual particles composed of many molecules. On evaporation of water, the particles come together. However, some combination of additional time and temperatures needed to fuse these particles to the same intimate molecular mixture as obtained from a solution [Fig. 7]. The ease of achieving this intimate fusion of particles is dependent upon the softening point of resins, the mutual solubility of the resin and polymer, and the relative particle size of the resin dispersion and polymer latex.

Effect of Tackifying Resin on Rheological properties of Elastomers

The effect of adding tackifiers on the rheological properties of elastomers has been investigated & the results are instructive in understanding how a tackifier functions. Fig. 8 shows a plot of shear storage modules G' of the natural rubber with & without a tackifying resin. When the resin is present, the resistance to deformation is reduced i e. lower G' at lower rates and hence, bond formation is facilitated on contact. At the same time, when measuring the strength of the bond, at higher rate of deformation, the module G' is high and the material is stronger. This behavior can be contrasted with effect of adding a filler or a simple plasticizer A filler would increase G' over the entire range of rate of deformation, leading to difficulties in bond formation simple plasticizers lower the cohesive strength of the adhesive. Thus a tackifiers an appropriate comprises substance that

facilitates bond formation and increases the elastic module and therefore increases the strength during detachment.

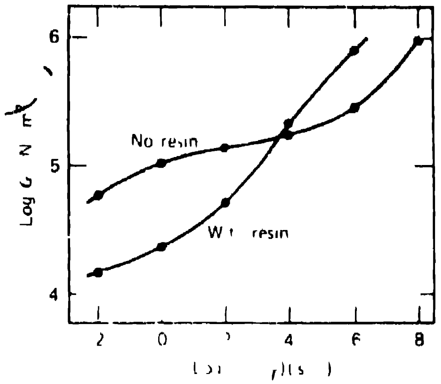


Figure 8 Effect of Tackifying Resin on the storage modulus of the natural rubber

SELECTION OF DISPERSION RESIN

The major factors in determining the type of resin to use with a particular polymer latex are resin composition or chemical structure and molecular weight. Using the concept of a resin functioning as a solid solvent for a portion of the polymer, similar solubility characteristics are necessary if the resin is to act as a tackifier[8] Low molecular weight resins will typically be better solvents for a given polymer than will high molecular weight resins Controlled solubility is necessary for good pressure sensitive adhesive performance. Resin solubility, then, is determined by both chemical structure and molecular weight Once mutual compatibility has been established, other factors, such as thermal and ultra violet stability, initial color and cost, become important in selecting a resin.

The three major backbone polymer that are currently used in emulsion pressure sensitive adhesives are natural rubber, Carboxylated SBR, and acrylics. The major types of resins used for tackifying each polymer.

NATURAL RUBBER

PETROLEUM ALIPHATICS

PETROLEUM AROMATICS

TERPENES

ROSINS ESTERS

CARBOXYLATED STYRENE-BUTADIENE RUBBER

ROSIN ESTERS

PETROLEUM AROMATICS

LOW MOLECULAR WEIGHT PURE MONOMER AROMATICS

ALPHA-PINENE TERPENES

ACRYLIC POLYMERS

ROSIN ESTERS

PURE MONOMER AROMATICS

LOW MOLECULAR WEIGHT POLYSTYRENES AND COPOLYMERS OF ALPHA-METHYLSTYRNE OR VINYLTOLUENE

POLYMER LATEXES

Properties that are of importance in a pressure sensitive elastomer latex include:

1.) Molecular weight
2.) Molecular weight distribution
3.) Glass transition temperature
4.) For styrene –butadiene rubber (SBR)elastomers ,the level of bound styrene

In SBR system, the styrene imparts cohesive strength to the polymer and thus to the finished adhesive.

Too much styrene in the polymer, however, will increase the glass transition temperature of the elastomer to a point where the flow of the formulated adhesive at room temperature and subsequent wetting of the substrate will be inhibited.

From previous viscoelastic studies, we know that pressure sensitive adhesive performance is dependent upon having the glass transition temperature of the resin-rubber blend within a specified temperature range. For example, room temperature, pressure sensitive adhesives will typically has glass transition temperature of approximately - 15 to +5 ^{0} C the desired glass transition temperature range is obtained by blending a high glass transition temperature hard resin with a low glass transition temperature elastomer.

Fig 9 shows curves obtained from a dynamic mechanical study of an acrylic-resin blend. The maximum in each curve corresponds to the glass transition temperature of the blend .The ability to modify glass transition temperature of the blend by varying resin level is apparent. Low glass transition temperature elastomer is desirable to give formulating latitude.

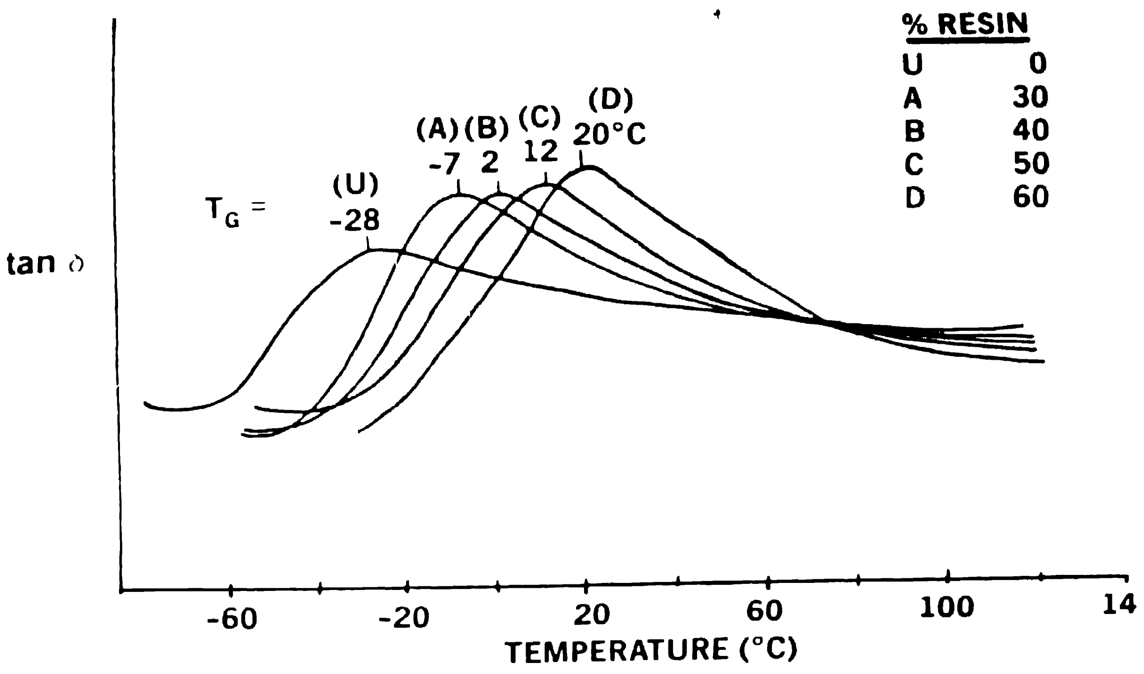


Fig. 9 EFFECT OF RESIN ON GLASS TRANSITION TEMP. OF AN ACRYLIC LATEX

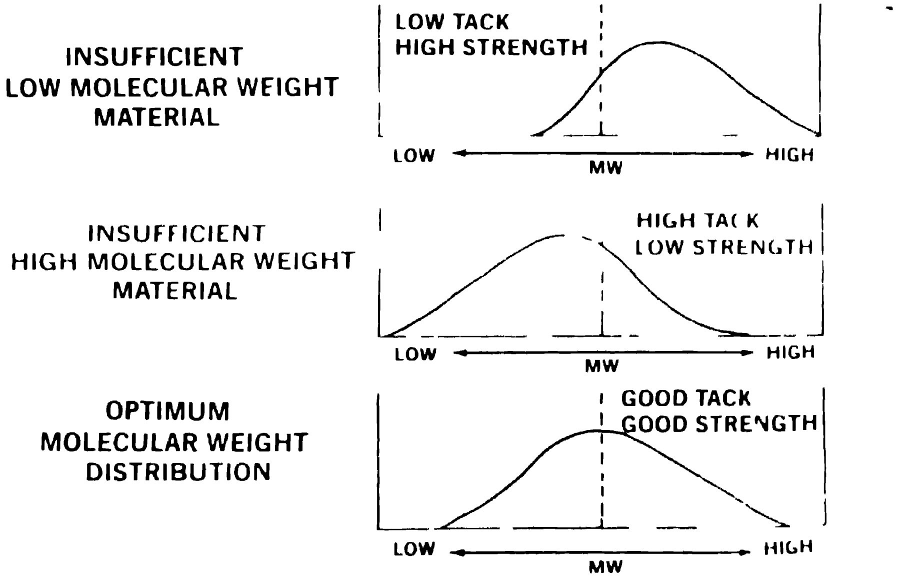


Fig. 10 EFFECT OF MOLECULAR WEIGHT DISTRIBUTION ON ADHESIVE PROPERTIES

Molecular weight distribution is also an important consideration in developing a latex. Elastomers with broad molecular weight distribution typically show better performance the materials with narrow molecular weight distribution. The concept of tackifying resins functioning as solid solvents for portions of the elastomer has been used for many years to explain the need for a broad molecular weight distribution. According to this theory, resins will dissolve the lower molecular weight fractions of the elastomer and create tack. The undissolved higher molecular weight fractions are needed to maintain the cohesive strength. Without a proper molecular weight distribution, the desired balance of the tack and strength cannot be obtained.

Fig. 10 shows this concept graphically. If there is a large amount of high molecular weight material, as shown in the top drawing, only a small amount of polymer will dissolve in the tackifying resin and only a low level of tack will be obtained. Even with low tack, however, cohesive strength will be high once a bond is established. If, on the other hand, there is a large amount of low molecular weight material but not much high molecular weight material, as shown in the middle drawing, the resin will dissolve a significant portion of the polymer to give a very tacky product, but there will be insufficient high molecular weight material to give strength to the adhesive. A broad, nearly symmetrical molecular weight distribution as shown in the bottom drawing, would be the most desirable.In this case,there will be enough high molecular weight material to give cohesive strength and sufficient low molecular weight material to generate the desired level of tack.

Styrene –butadiene rubber latexes have traditionally been used in paper coatings and backing applications. Typically, these latexes have had a high styrene content (approx., 37-54%) and therefore high glass transition temperature (-17 ° C and above). These latexes are usually high molecular weight polymers, difficult to tackify and are generally unsuitable for pressure sensitive adhesive applications. Some evaluations have found the most effective SBR latexes to be those wit a bound styrene level of 25-35 % and glass transition temperature in the range of -45 to -35°C.A broad molecular weight distribution is assumed to be contributing to the effectiveness of these latexes.

ADHESIVE PERFORMANCE

In order to illustrate the effect of polymer latex properties on performance, pressure sensitive adhesive performance data have been obtained on a variety of polymer latexes.

Fig. 11 through 13 show the properties obtained with three carboxylated SBR latexes supplied by one producer when formulated with a dispersion of floral 85 rosin ester. These latexes have the same styrene content (35%) and the same glass transition temperature (-32° C). According to information from the producer, the three latexes differ, however, in molecular weight and molecular weight distribution

Latex A is a high molecular weight polymer .It does not appear to have a sufficient amount of lower molecular weight material to generate much tack, as seen from the low values for 90 degree quickstick and polyken tack. Even though there is a little aggressive tack in these formulations, the

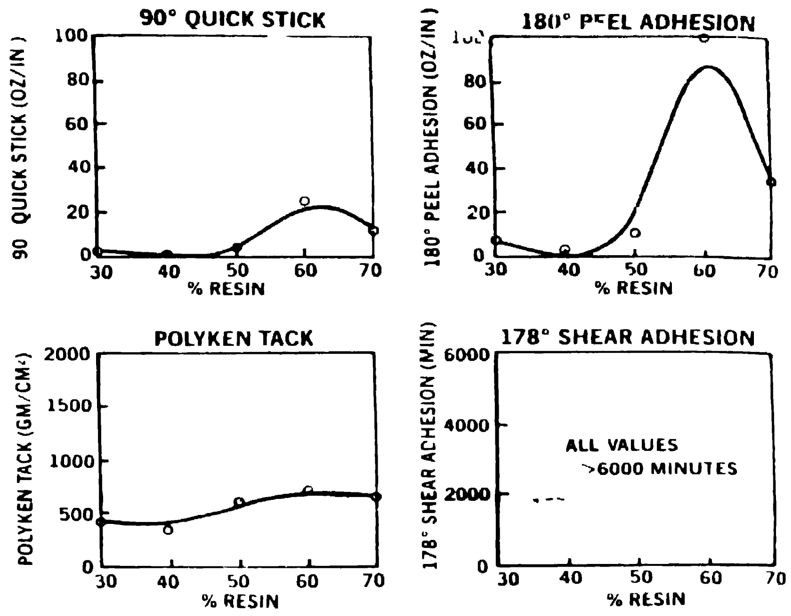


Fig. 11 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF FORAL 85/CARBOXYLATED SBR LATEX A

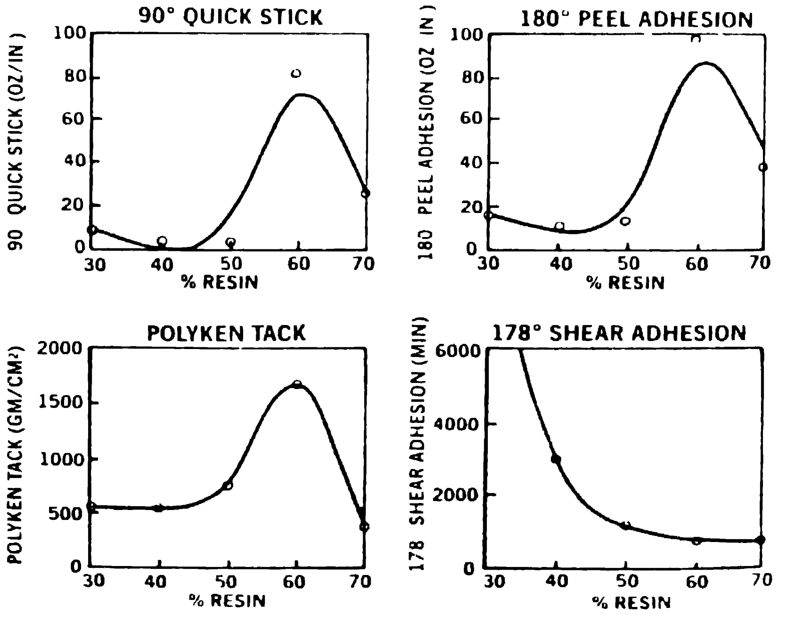


Fig. 12 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF FORAL 85/CARBOXYLATED SBR LATEX B

application of pressure to the tape results in a reasonable 180-degree peel value and excellent 178 degree shear adhesion.

Latex B is a low molecular weight polymer. From the 90-degree quickstick and polyken tack curves, we can see that there is an improvement in the development of tack over latex A.However, Latex B does not contain enough high molecular weight material to maintain cohesive strength, as evidence by the drop-off in 178-degree shear adhesion as the resin loading increases. Much of the polymer appears to be dissolved by the resin, resulting in the loss of cohesive strength.

Latex C appears to have a better balance of properties. The presence of high molecular weight components is shown by the excellent 178-degree shear adhesion, while the presence of low molecular weight components is shown by the higher levels of 90-degree quickstick and 180-degree peel compared to latex A.

Latex C would give the adhesive compounder broader formulating latitude than would be possible with either Latex A and Latex B It is important to have this formulating latitude so that the compounder can achieve a wide range of adhesive properties with only a few base latexes. However, in a case where very high levels of tack or shear adhesion are required, Latexes A and b could be useful materials. The choice of a particular latex will obviously be determined by the end use application

Fig. 14 through 16 show the performance data obtained with three other SBR latexes supplied by a second producer. Latexes D and E were not designed primarily for pressure sensitive adhesive applications, while Latexes F has been specifically designed for use in pressure sensitive

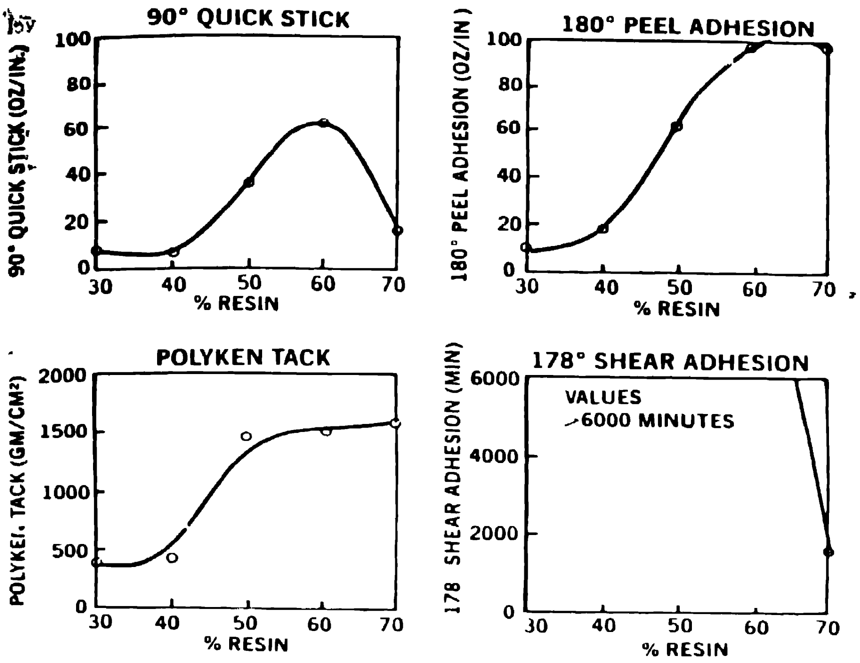


Fig. 13 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF FORAL 85/CARBOXYLATED & SBR LATEX C

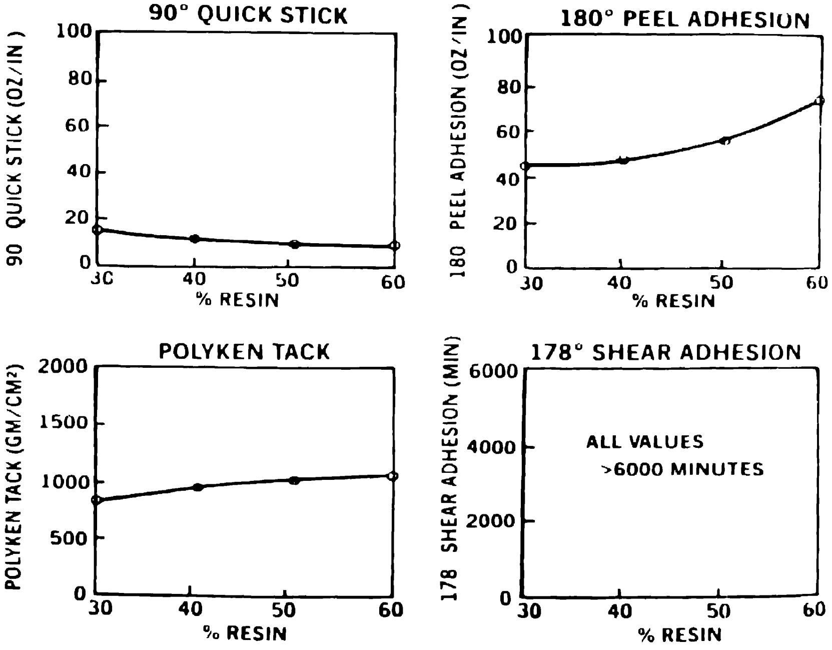


Fig. 14 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF FORAL 85/CARBOXYLATED & SBR LATEX D

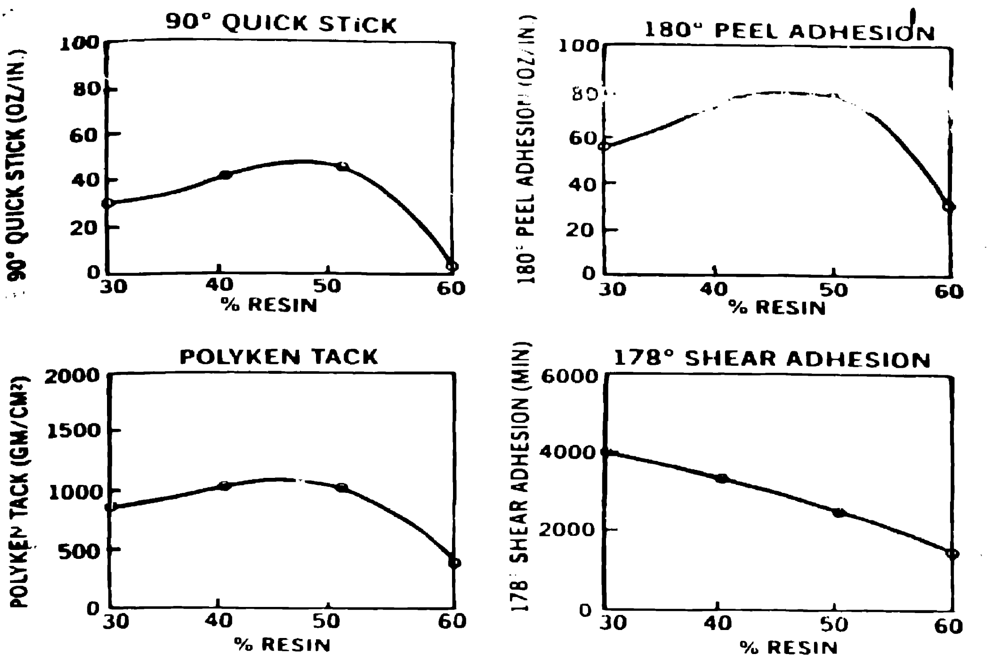


Fig. 15 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF FORAL 85/CARBOXYLATED LATEX E

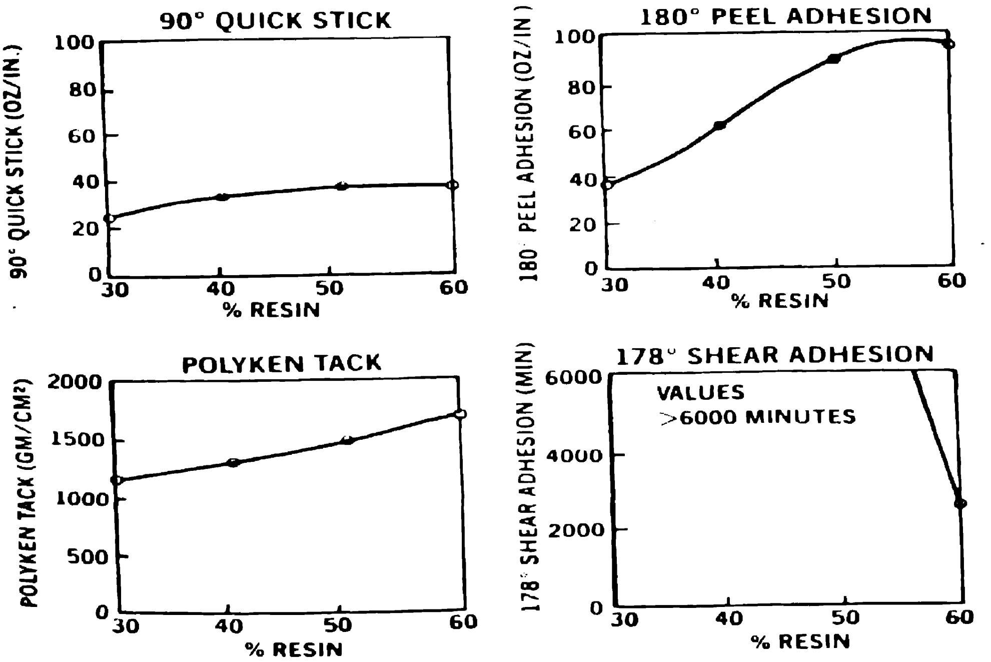


Fig. 16 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF FORAL 85/CARBOXYLATED LATEX F

adhesives. The tackifying resins used in latexes D and E was floral 85,while staybelite ester 10 was used with Latex F.

Latex D (Fig.14), a high molecular weight latex,contains a high level of styrene (46%) and therefore has a high glass transition temperature (-17 ° C) .This latex does not respond well to resin addition .Tack values are low but ,as we saw in the previous data,shear adhesion is good.

Latex E (Fig.15) is also high in styrene content (44%) and in glass transition temperature (-18 ° C). It's molecular weight and molecular weight distributions are such that it has a substantial amount of low molecular weight material, but an insufficient amount of higher polymer to provide strength. Therefore, as tack begins to increase upon resin addition,there is a decrease in shear adhesion .In addition ,the optimum level of tack is reached at a lower resin level than found in latexes A,B and C.This is due to smaller proportion of butadiene.The tack results from the association of resin and butadiene.In the region of optimum tack,the maximum amount of resin that the butadiene can hold has been added.Once this level is reached,the resin act only as a filler,and tack begins to fall off.Latexes with increased levels of butadiene can incorporate more resin before this maximum is reached.

From the standpoint of formulating pressure sensitive adhesives properties, latex F (Fig. 16) represents an improvement over Latexes D and L.The lower level of styrene (255), lower glass transition temperature, (-46 ° C), and broader molecular weight distribution allow for the development of good tack properties without a sacrifice of shear adhesion.

The adhesive properties discussed thus far have all been developed with carboxylated SBR latexes. Acrylic latexes will also respond to resin tackification. Acrylics have typically been used in solvent systems with very

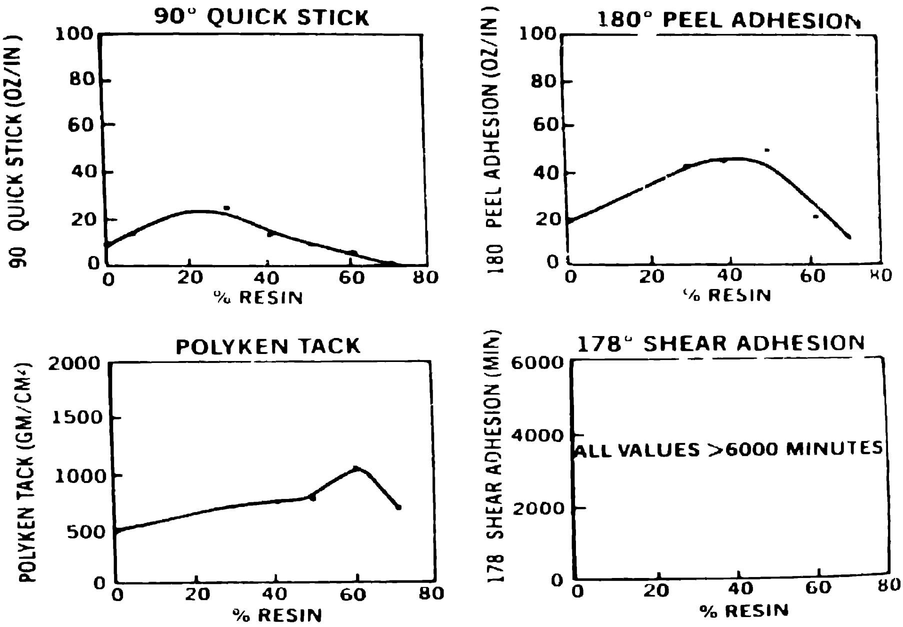


FIG. 17 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF STAYBELITE ESTER 10/ACYLIC LATEX G

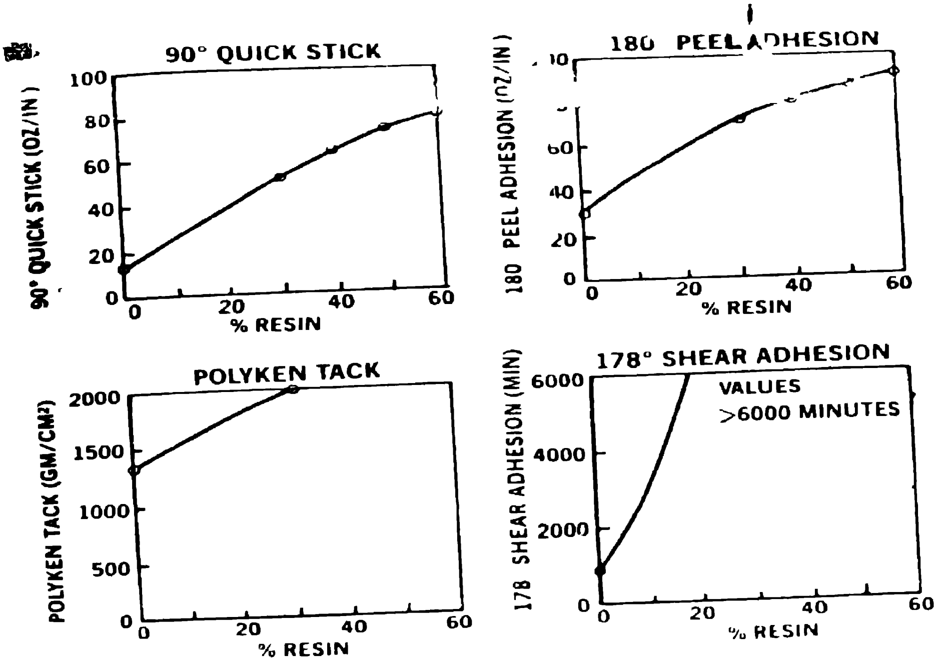


FIG. 18 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF PICCOTEX 75/ACRYLIC LATEX H

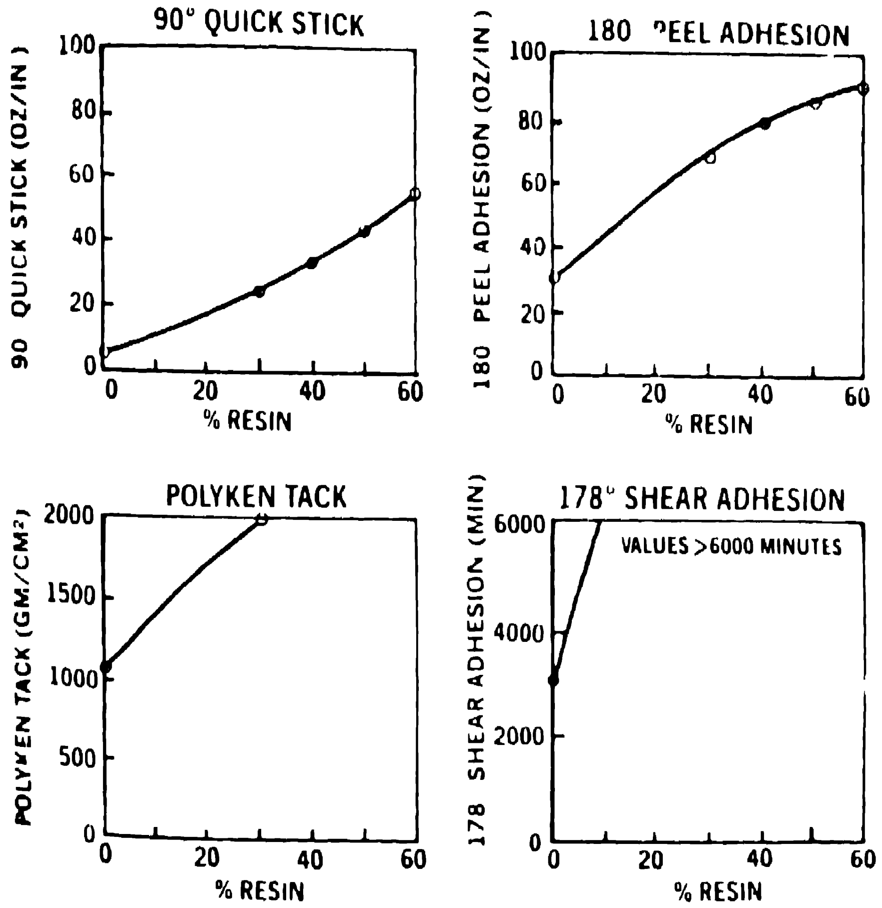


Fig. 19 PRESSURE SENSITIVE ADHESIVE PERFORMANCE OF PICCOVAR/ACRYLIC LATEXI

little or no tackifying resins. This is because a certain level of pressure sensitive adhesive properties can be built into an acrylic polymer. However, acrylic performance can usually be enhanced by resin modification. In addition, with so many different pressure sensitive adhesive applications, it would be impractical to design a polymer for each one. It is more reasonable to design a polymer or several polymers that can be modified for various applications through resin modification.

Fig. 17 shows the response of one particular acrylic latex (latex G) to resin tackification by staybelite Ester 10.This polymer was designed to give high shear adhesion. Upon resin addition, there is a significant improvement in 90-degree quickstick and 180-degree peel. The improvement in tack is accomplished with no loss of shear adhesion.

Fig. 18 and 19 show the response of two other acrylic latexes to resin tackification. In both cases, we see an increase in pressure sensitive adhesion properties over the unmodified latex. Through resin modification,the range of pressure sensitive adhesion properties that can be obtained with the polymer latexes has been extended.

The solvent free system offer various advantages over emulsion which utilize solvent to dissolve the resin

1.) Ability to produce lower viscosity adhesives, as one avail the thickening action of the solvent.
2.) Higher resin content.
3.) Addition of flammable solvents is averted.

4.) Greater latitude in controlling rheology with synthetic thickness is gained by omission or reduction of the amount of solvent, soap, and casein usually present in the emulsion.

5.) Environment friendly.

Major Applications of tackifying Resins

The main use of tackifying resins in adhesives is to improve the performance properties of hot melt, PSA and general purpose.

1.) Pressure sensitive adhesive

2.) Hot melt adhesive

3.) General purpose adhesive

4.) Food packaging application

Pressure sensitive adhesive: - Tackifying resins are used in **Pressure sensitive adhesive** which are used in tapes labels and decals and packaging .It is specially used for improving adhesion to low surface energy substrate example adhesion to HDPE, PE, preinsulation tapes, medical tapes.

Hot melt adhesive: -Tackifying resins are used in Hot melt adhesive. Hot melt adhesive are used in paper laminates, non woven books binding, labels, case, carton, trays, pet bottles, bags. Packaging contains such as case, cartons and trays both manufacture and closure are the largest application for Hot melt adhesive.

General purpose adhesive: - Tackifying resins are used in General purpose adhesive which in turn are used in labels, decals and tapes.

Food packaging: - Tackifying resins are also used in food grade packaging application.

Comparison between tackifying with water based tackifier & tackifying with solvent based tackifier

Tackifying with water-based tackifiers

From a technical point of view this remains the most simple technology. Demixing problems during feed-in can be avoided. No special knowledge for the converter is needed. The coating properties (wetout, mechanical stability) are the best; no flammable agents are used. Current dispersion coating machines may be used without special precautions.

On the other hand, aqueous resin-tackifier dispersions show some weakness also. These can effect the properties of the final coating in areas such as a lower water resistivity of the coating,a lower anchorage of the adhesives higher penetration or bleeding of the adhesive,lower shear and poorer die cutting.The water-based resin dispersions are secondary dispersions made with surface active agents(2-14%).This additional amount of surface active agent in the final coating increases its solubility and hygroscopy.Concerning the influence of the emulsion character of the tackifier on the adhesive properties ,there are divergent data in the literature.It is assumed that the adhesive properties of the tacikified PSAs are inferior to those of solvent-based resin-tackified PSAs.This hypothesis is illustrated by the limited amount of tackified water-based PSAs for film coating.In this case the loading of the tackifier remains limited(< 10%).Therefore , solvent –based tackifier are used more often.On the other hand,it was shown that with the exception of a slight change in rolling ball tack,there is little difference between the same adhesives coated with water and solvent carriers.

Tackifying with Solvent –based Tackifiers

Solvent based tackification is an old technology enjoying some renaissance because of the superior water resistivity and tack of solvent-based resin tackified coatings. The anchorage of the directly coated solvent-based resin tackified coatings also appear superior. Unfortunately there are some technological disadvantages associated with solvent –based resin tackifying. First, the manufacture of the concentrated (70-80 %) resin solutions causes difficulties for a converter without chemical knowledge. Furthermore, the formulation(feed-in)technology for the resins solution in the aqueous dispersion requires special knowledge and equipments.Because of the low level of surface-active agents the mechanical stability of solvent-based resin-tackified dispersions is low;the wetout of the dispersion is inferior and generally does not allow transfer coating on solventless silicones.Theoretically,no special converting machines are required for solvent –based resin-tackified formulations;practicaly,some precautions are needed.Except for the water resistivity ,no improvement in the peel/tack/shear balance for solvent-based tackified water-based acrylic PSAs is observed.

References :

1. Casey A.Z., Water based pressure sensitive adhesives-Formulation & performance. Presented by A. yoshioka at Japan , Pressure sensitive tape association meeting Nov. 1985.
2. Encyclopaedia of polymer Science vol. 1.
3. Handbook of pressure sensitive adhesive technology by D. satas,james a. schlademan,The Goodyear Tire & Rubber Company,Akron,Ohio.
4. The condensed Chemical dictionary 9th edition [Revised by G.G. Hawley], Van Norstrand Reinhald, New York, 1977.
5. Shaw D.J., Introduction to colloid 7 surface chemistry, 2nd edition, Butterworth, Boston, 1970.
6. Beneth H., Bishop J.L. jr., & Wulfinghoff M.L., Practical Emulsions, vol. 1,materials & Equipment's, Chemical Publishing House, New York, 1968.
7. Linsay E.C., Aqueous Resin Dispersions presented at ASTM D-14 Water based systems seminar Boston, Massachusetts, Oct.1977.
8. Zawilinski, A Water based, pressure sensitive adhesive formulation 7 performance presented at the Pressure Sensitive Tape Council Technical seminar, Chicago, 3rd May 1984.
9. Benedek I., Heymants L.J., Pressure sensitive adhesives technology, Marcel Dekker Inc., New York.